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(54) Organometallic complexes of aluminium, gallium and indium

(57) Novel organometallic complexes of aluminium, gallium and indium are disclosed, having improved stability and volatility for use in CVD processes. These are donor ligand complexes of the formula RM.L₂ where M is the metal, R is an alkyl group and L is a ligand containing an amidine (R'N—C(R')—NR') group, where R' is H, alkyl etc.

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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

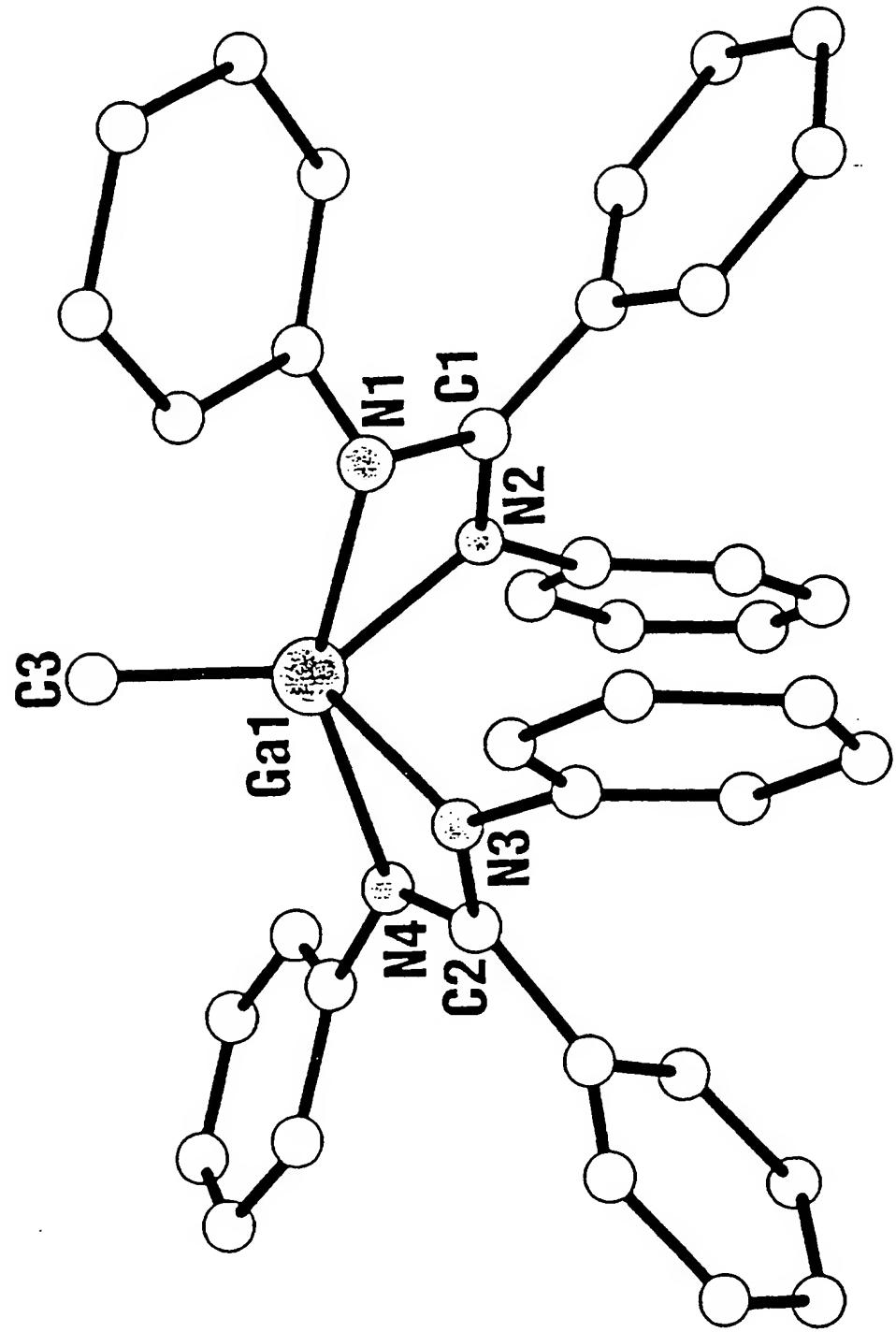
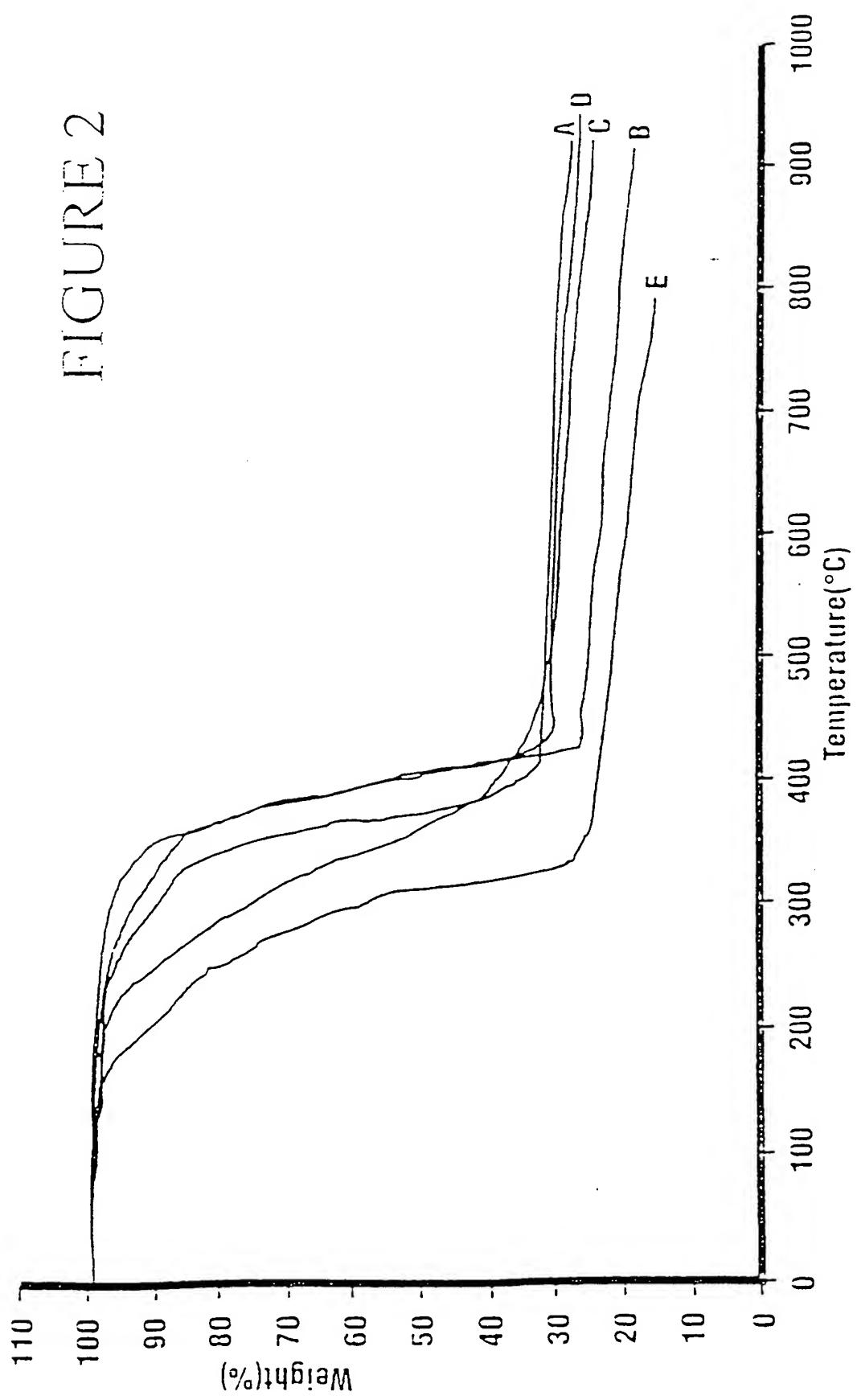


FIGURE 1



ORGANOMETALLIC COMPLEXES
OF ALUMINIUM, GALLIUM AND INDIUM

This invention relates to volatile organometallic complexes of aluminium, gallium and indium.

Volatile organometallic compounds of aluminium, gallium and indium, e.g. the aluminium, gallium and indium alkyls, especially trimethyl gallium and triethyl indium, are of considerable interest as volatile sources of aluminium, gallium and indium metal in CVD (chemical vapour deposition) processes. Of particular interest are CVD processes employing a volatile source of aluminium, gallium or indium in the manufacture, by chemical vapour deposition on the surface of a suitable substrate, of compound semi-conductor materials such as gallium arsenide (GaAs), indium arsenide (InAs), indium phosphide (InP), indium aluminium gallium arsenide (InAlGaAs) or wide bandgap material systems such as aluminium, gallium or indium nitride.

Metal alkyls, such as trimethylaluminium, trimethylgallium and triethylindium, are, however, unstable at elevated temperature, pyrophoric and extremely sensitive to air, and are explosively hydrolytic in contact with moisture. Such materials can, therefore, be manufactured and used only under very stringent conditions.

In accordance with the present invention we have discovered that the amidine complexes of aluminium, gallium and indium dialkyls possess good stability at room temperature, are substantially non-pyrophoric, and show excellent thermal stability in the vapour phase. They are, therefore, of high utility as a volatile source of aluminium, gallium and indium in CVD processes of all kinds.

In accordance with the present invention, therefore, there are provided novel organometallic complexes of the Formula I

where M is aluminium, gallium or indium, R is C₁-C₈ alkyl, preferably methyl or ethyl; and L is an organic ligand containing a substituted or unsubstituted amidino [R'N---C(R')---NR'] group.

5 Preferred amidine ligands are amidines of the Formula II:



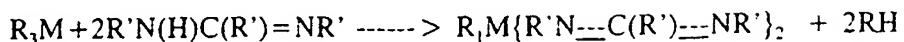
10 where R' is H, C₁-C₈ alkyl or haloalkyl, C₃-C₈ cycloalkyl, optionally including an -NH- group in the ring, C₃-C₈ cycloalkenyl, phenyl or substituted phenyl containing from 1-3 (C₁-C₈)alkyl or halo-substituents, trimethylsilyl or halogen, the R' groups being the same or different.

15 Typical amidine ligands within that formula are N,N'-diphenylbenzamidine, N,N'-di(p-chlorophenyl)acetamidine, N,N'-diphenylformamidine, N,N'-di(p-fluorophenyl)acetamidine, benzamidine, acetamidine, and N,N'-dicyclohexylacetamidine. Other suitable amidine ligands will be apparent to those skilled in the art, as will be methods for the preparation of such amidines.

20 The advantages of the complexes of the present invention are that the reduced alkyl content of the complex reduces significantly the possibility of carbon inclusion in the deposited product. Also, the complexes are useful for the polymerisation of acrylic monomers, being similar to enolate - aluminium porphrin complexes known to those skilled in the art, but having the distinct advantage of not requiring an expensive 25 porphrin constituent.

30 The amidine complexes of this invention can be prepared by reacting a suitable amount of the trialkylaluminium, trialkylgallium or trialkylindium compounds, e.g. trimethylaluminium, trimethylgallium or triethylindium with the ligand under anhydrous conditions *in vacuo* or under an inert atmosphere, preferably, but not necessarily in the presence of an anhydrous hydrocarbon solvent such as toluene or n-hexane. That reaction may be represented as follows:

vacuo/inert gas



5

The alkane (RH) evolved during the course of the reaction is removed preferably continuously, following which the product complex can be recovered by removal of the excess aluminium, gallium or indium trialkyl and the solvent, if present, preferably by distillation *in vacuo*.

10

Whilst the alkyl substituents of the aluminium, gallium or indium trialkyl reactant will usually be the same, trialkyls containing different alkyl groups may be used.

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Aluminium, gallium and indium complexes in accordance with this invention and the preparation thereof will now be described by way of examples. In this regard, reference is made to the following Figures, in which:

Figure 1 is the crystal x-ray diffraction results for $\{MeGa(NPhCPhNPh)_2\}^{III}$; and

20

Figure 2 shows the thermogravimetric analysis curves of various complexes according to the invention.

In all the Examples, the reactions were carried out on a vacuum line.

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Synthesis of $\{MeGa(NPhCPhNPh)_2\}^{III}$

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N,N'Diphenylbenzamidine (2.28g, 8.4 mmol) was dissolved in dry degassed toluene, and GaMe₃ (0.49g, 4.25 mmol) was distilled in under vacuum. The stirred solution was allowed to warm to room temperature, over which time methane (95cm³, 4.25 mmol) was evolved. The solution was heated to 100°C for 12 hours, evolving further methane, allowed to cool to room temperature and reduced in volume to ca. 20 cm³ under vacuum. Hexane (30cm³) was added and the air sensitive pale yellow precipitate was isolated by filtration.

Yield 1.8g (68%).

Found: C, 74.62; H, 5.35; N, 8.93%

$C_{39}H_{33}N_4Ga$ requires C, 74.66; H, 5.30; N, 8.93%

5

1H NMR ($CDCl_3$): d 7.19 (p-ArH-C, 2H, t, 6Hz), 7.14 (o-ArH-C, m-ArH-C, 8H, d, 4Hz), 6.95 (m-ArH-N, 8H, t, 8Hz), 6.83 (p-ArH-N, 4H, t, 7Hz), 6.57 (o-ArH-N, 8H, d, 8Hz), 0.28 (GaCH₃, 3H, s).

10

^{13}C NMR ($CDCl_3$): 167.96 (N-C-N), 144.90 (Ar-N), 130.70 (Ar-C), 129.82 (p-Ar-C), 129.31 (o-Ar-C), 128.05 (m-Ar-C), 127.96 (m-Ar-N), 124.96 (o-Ar-N), 122.22 (p-Ar-N). -8.0 (R₁)

15

M.S. (EI), 626(M⁺, 7.8), 611([M-Me]⁺ 43.4), 355([M-PhNCPh NPh]⁺, 13.5), 180 ([PhNCPh]⁺, 100%).

The product may also be purified by sublimation under vacuum at 100°C. Single crystal x-ray diffraction studies bipyramidal geometry with two bidentate chelating amidinato ligands - see Figure 1.

20

Synthesis of $\{[MeAl(PhNCPhNPh)_2]^{III}$

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N,N'-Diphenylbenzamidine (1.18g, 4.3 mmol) was suspended in dry degassed hexane (30 mls), cooled to -78°C and a solution of AlMe₃, in hexanes (1.1 mls, 2 M) was added via syringe. The stirred solution was allowed to warm to room temperature and stirred for a further two hours. The resulting white suspension was cooled at 0°C for 30 minutes and the air sensitive solid isolated via filtration and dried under vacuum for 2 hours. The product may also be purified by sublimation under vacuum at 100°C.

30

Yield 0.94g (75%).

Found: C, 80.13; H, 5.90; N, 9.55%.

$C_{39}H_{33}N_4Al$ requires C, 80.11; H, 5.69; N, 9.58%.

1H NMR ($CDCl_3$): δ /ppm 7.17 (ArH, 2H, t, 8Hz), 7.12 (ArH, 8H, t, 8Hz), 6.95-6.79 (ArH, 12H, m), 6.54 (ArH, 8H, d, 7Hz), -0.36 (Al-Me, 3H, s).

^{13}C NMR ($CDCl_3$) : 170.83(N-C-N), 143.99(Ar-N), 129.78(Ar-C), 129.67(p-Ar-C), 128.10(M-Ar-C), 127.9(M-Ar-C), 124.55(o-Ar-N), 132.47(p-Ar-N), -12.03(Al-Me).

Single crystal x-ray diffraction studies showed the compound to be iso-structural with the Gallium derivative.

Synthesis of $\{MeAl(PhNCMeNPh)_2\}^{III}$

This complex was prepared by the same procedure as used for methylaluminium-bis(N,N^1 -diphenylbenzamidinato). A hexane solution of Al_2Me_6 ($1.38cm^3$, 1.38mmol) was added to a suspension of N,N^1 -diphenylacetamidine (1.16g, 5.52mmol) in hexane ($40cm^3$). The product was a colourless crystalline solid.

Yield: 0.87g (69%).

Analysis requires $C_{29}H_{29}N_4Al$:C, 75.63;H, 6.35; N,12.16%.

Found: C, 75.89,H,6.43;N,12.10%.

1H NMR ($CDCl_3$): δ /p.p.m. -0.26 (s, 3H, $AlCH_3$), 2.05(s, 6H, CH_3), 6.80(d,8H, o-ArH-N.), 6.96 (t,4H, p-ArH-N), 7.11 (t, 8H, m-ArH-N.).

Synthesis of $\{EtGa[PhNCMeNPh]_2\}^{III}$

N,N^1 -Diphenylacetamidine (0.90g, 4.28mmol) was slowly added to a stirred solution of Et_3Ga (0.34g, 2.16mmol) in hexane ($40cm^3$) at room temperature, whereupon gas was immediately evolved and the reaction mixture was left to stir for 1 hour.

After this time the suspension was heated to 70°C for 12 hours and then allowed to cool. This produced a colourless solution that was concentrated under reduced pressure until precipitation of a white microcrystalline solid occurred. The product was recrystallised from hot hexane solution, producing large colourless block-shaped X-ray diffraction quality crystals, which were isolated by filtration and dried in vacuo.

Yield: 0.82g(74%)

Analysis, C₃₀H₃₁N₄Ga requires: C, 69.65; H, 6.04; N, 10.83%.

Found: C, 67.99; H, 6.01; N, 10.58%.

¹H NMR (CDCl₃) require: δ/p.p.m. 1.12(q, 2H, GaCH₂CH₃), 1.42(t, 3H, GaCH₂CH₃), 2.08 (s, 6H, CH₃), 6.82(d, 8H, o-ArH-N,), 7.00(t, 4H, p-ArH-N,), 7.17(t, 8H, m-ArH-N).

M.S.(EI): S17(M⁺, 1.9), 488([M-Et]⁺, 65.7), 118 ([PhNCMe]⁺ 100%)

¹³CNMR (CDCl₃): 167.29 (N-C-N), 146.35 (Ar-N) 128.52 (m-Ar-N), 124.52 (o-Ar-N), 122.37 (p-Ar-N), 15.26 (C-CH₃), R, CH₃ 11.93, CH₂ 5.86.

Synthesis of {EtIn(PhNCPhCPh)₂} ^{III}

This complex was synthesised using a similar procedure to that used for the ethylgallium-bis(N,N¹-diphenylacetamidinatol complex above. N,N¹-Diphenylbenzamidine(1.39g, 5.10mmol) reacted with a solution of Et₃In(0.52g, 2.57mmol) in hexane (30cm³). After heating at 80°C for 4 hours, a white suspension was obtained, which was isolated by filtration and dried in vacuo.

Yield: 1.10g (62%).

Analysis, requires $C_{40}H_{35}N_4In$ (requires): C, 69.98; H, 5.13; N, 8.16%.
 Found: C, 70.09; H, 5.12, N, 8.12%.

1H NMR ($CDCl_3$): δ /p.p.m. 1.25 (q, 2H, $InCH_2CH_3$), 1.46(t, 3H, $InCH_2CH_3$), 6.51(d, 8H, o-ArH-N), 6.82(t, 8H, p-ArH-N), 6.95(t, 8H, m-ArH-N) 7.10-7.26 (m, 10H, p-ArH-C, o-ArH-C, m-ArH-C).

Crystals of this complex suitable for the X-ray structural analysis carried out were grown from hexane solution at -35°C.

^{13}C NMR ($CDCl_3$): 168.28 (N-C-N), 146.13(Ar-N), 132.03 (Ar-C), 129.96 (p-Ar-C), 128.96 (o-Ar-C), 128.02 (m-Ar-C), 128.02 (m-Ar-N), 124.85 (o-Ar-N), 121.79 (p-Ar-N), R, CH_3 11.90, CH_2 6.28.

Synthesis of $[EtIn(PhNCMeNPh)_2]$

This complex was also synthesised using a similar procedure to that used for the ethylgallium-bis(N,N^1 -diphenylacetamidinato) complex above. N,N^1 -Diphenyl acetamide (1.39g, 6.61mmol) was reacted with a solution of Et_3In (0.67g, 3.32mmol) in hexane (30cm $_3$). After heating at 80°C for 4 hours, the colourless solution was left to cool to room temperature, producing a colourless crystalline solid.

Yield: 1.24g (67%)

Analysis: $C_{30}H_{31}N_4In$ requires C, 64.98%; H, 6.13, N, 9.47%.
 Found: C, 65.04, H, 5.65; N, 9.68%.

1H N.M.R. ($CDCl_3$): δ /ppm; 1.18 (q, 2H, $InCH_2CH_3$), 1.47 (t, 3H, $InCH_2CH_3$), 2.10 (s, 6H, CH_3), 6.80 (d, 8H, o-ArH-N), 6.99 (t, 4H, p-ArH-N), 7.17 (t, 8H, m-ArH-N).

1). Thermal Decomposition Studies: Example GaN production.

Samples were heated to 600°C under a nitrogen atmosphere in a silica tube contained in a thermostatically controlled furnace. The optimum decomposition temperature was determined from the t.g.a. data which was also obtained under a nitrogen atmosphere. The residual grey powder was stored under nitrogen. Electron microscopy revealed domains of GaN, many of which were on the surface of background carbon particles. X-ray powder diffraction data showed d(Å) lines at 2.79, 2.58, 2.43, 1.59, 1.46, 1.38 characteristic of GaN. Energy dispersive X-ray spectroscopy (EDX), obtained using 5 keV electron beam with a Cambridge S250 instrument with a link analytical X-ray system using an LZ5 Windowless detector, showed X-ray emissions corresponding to the L and K shell of gallium and nitrogen respectively, together with smaller emissions corresponding to carbon and oxygen.

15 2). Catalysis Studies:

The (TGA) thermogravimetric analysis curves of various complexes according to the present invention are shown in figure 2 and the complexes to be thermally stable to at least 175°C, (e.g. curve E), allowing ease of handling at ambient and elevated 20 temperatures. The curves also show the materials lose the ligand in a single clean step at higher temperatures. The following key applies:

25 Curve A: EtIn(N,N¹ diphenylacetamidine)₂
Curve B: EtIn(N,N¹ diphenylbenzamidine)₂
Curve C: EtGa(N,N¹ diphenylbenzamidine)₂
Curve D: MeIn(N,N¹ diphenylbenzamidine)₂
Curve E: MeAl(N,N¹ diphenylbenzamidine)₂

30 Thus the complexes may be readily volatalised intact, and have a useful thermal stability range; both of which properties make them useful metal precursors in metal CVD operations. Further, observation of parent ions in the mass-spectra of these complexes may be thought indicative of the thermal-stability-volatility of such

complexes under vacuo and thermal load.

The thermal decomposition studies described are merely illustrative of the usefulness of these materials for metal nitride production and should not be viewed as limitative.

5

Other modifications of the present invention will be apparent to those skilled in the art.

CLAIMS:

1. Organometallic aluminium, gallium and indium complexes of the formula I:

5

RM₂L₂

I

wherein

M is aluminium, gallium or indium;

10 R is C₁-C₈ alkyl, the two R groups being the same or different; and

L is an amidino group of the formula II

R'N—C(R')—NR'

II

15

wherein

R' is H, C₁-C₈ alkyl or haloalkyl, C₃-C₈ cycloalkyl optionally including an NH- group in the ring, C₃-C₈ cycloalkyl, phenyl, substituted phenyl containing from 1-3 (C₁-C₅) alkyl or halo-substituents, trimethylsilyl or halogen, the R' groups being the same or different.

20
2. Organometallic aluminium, gallium and indium complexes according to claim 1, where R is methyl or ethyl.

25

3. Organometallic aluminium, gallium and indium complexes according to claim 1 or claim 2 wherein the amidine group is derived from any one of the following: acetamidine, benzamidine, N,N'-diphenylbenzamidine, N,N'-di(p-chlorophenyl)acetamidine, N,N'-diphenylformamidine, N,N'-diphenylacetamidine, N,N'-di(p-tolyl)benzamidine, N,N'-di(p-fluorophenyl)acetamidine, and N,N'-dicyclohexylacetamidine.

4. A method for the chemical vapour phase deposition of aluminium, gallium or indium on a substrate which comprises contacting the substrate with a volatile organometallic gallium or indium in the vapour phase, wherein there is used an organometallic aluminium, gallium or indium complex according to any one of claims
5 1 to 3.

5. A compound substantially as described herein.

6. A ~~compound~~^{*method*} substantially as described herein.



The
Patent
Office
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Application No: GB 9523993.5
Claims searched: 1-4

Examiner: Roy Honeywood
Date of search: 31 January 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): C2J (JJC)

Int CI (Ed.6): C07F

Other: ONLINE: CAS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	None	

X Document indicating lack of novelty or inventive step	A Document indicating technological background and/or state of the art.
Y Document indicating lack of inventive step if combined with one or more other documents of same category.	P Document published on or after the declared priority date but before the filing date of this invention.
& Member of the same patent family	E Patent document published on or after, but with priority date earlier than, the filing date of this application.